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Iron–Sulfur Interactions within Azathiaferrocenophanes. Synthesis and Electrochemistry of Azathiaferrocenophanes and Their Acyclic Analogues

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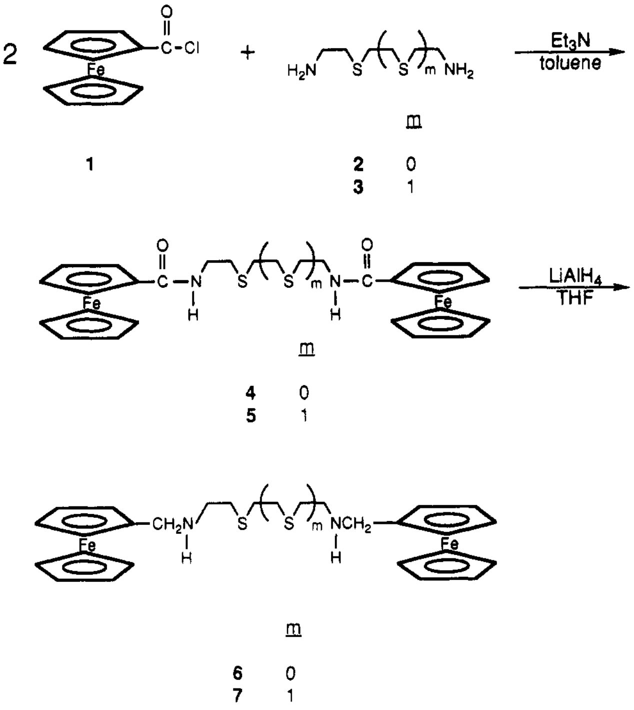
N,N-Didecyl-2,8-diaza-5-thia[9](1,1′) ferrocenophane (**20**), *N,N*-didecyl-2,11-diaza-5,8-dithia[12](1,1′) ferrocenophane (**21**), and acyclic analogues in which the bridging units link two ferrocenyl moieties have been prepared. Compared with the acyclic analogues and with *N,N*-didecyl-2,11-diaza-5,8-dioxa[12](1,1′) ferrocenophane (**22**) the half-wave reduction potentials for **20** and **21** in acetonitrile are 0.3 V more positive, which demonstrates stabilization of the Fe(II) oxidation state by a thioether sulfur atom of the azathiaferrocenophane.

Introduction

A variety of crown ether like ferrocenophanes containing various heteroatoms have been described.[1–12] Among them, polyoxathiaferrocenophanes that bind alkali-metal cations were studied most extensively. Ferrocenophanes that contain sulfur as the only ring heteroatom have also been reported.[8,9] Trithiaferrocenophanes ligate copper(I), silver(I), mercury(II), and palladium(II) in complexes where the possibility of metal–metal interaction with the ferrocene Fe atom is of particular interest.[10–12] For the class of ferrocenophanes that contain both nitrogen and sulfur heteroatoms, only a single example, a diazadithiaferrocenophane diamide, was reported very recently.[7] In this paper, we describe the synthesis and electrochemical properties of a diazathiaferrocenophane and a diazadithiaferrocenophane. For comparison acyclic analogues of the two azathiaferrocenophanes are also prepared, as well as a new diazadioxaferrocenophane. Although the synthesis of heterobimetallic adducts from azathiaferrocenes provided the original incentive for this work, unexpected trends in ferrocenium/ferrocene half-wave potentials which point to strong Fe–S interactions within the parent compounds have proven to be equally interesting.

Scheme I



Results and Discussion

Synthesis. Acyclic ferrocene thiadiamines **6** and **7** were prepared by the reaction sequence outlined in Scheme I. Reaction of ferrocenoyl chloride[13] (**1**) with thiadiamine **2**[14] and dithiadiamine **3**[15] in the presence of triethylamine afforded diamides **4** and **5** in 72 and 67% yields, respectively. Reduction of the diamides with lithium aluminum hydride in tetrahydrofuran produced acyclic ferrocene thiadiamines **6** and dithiadiamine **7** in 78 and 62% yields, respectively.

When difunctional 1,1′-bis(chlorocarbonyl)ferrocene[16] (**8**) and thiadiamine **2** and dithiadiamine **3** were condensed under high-dilution conditions in the presence of tri-

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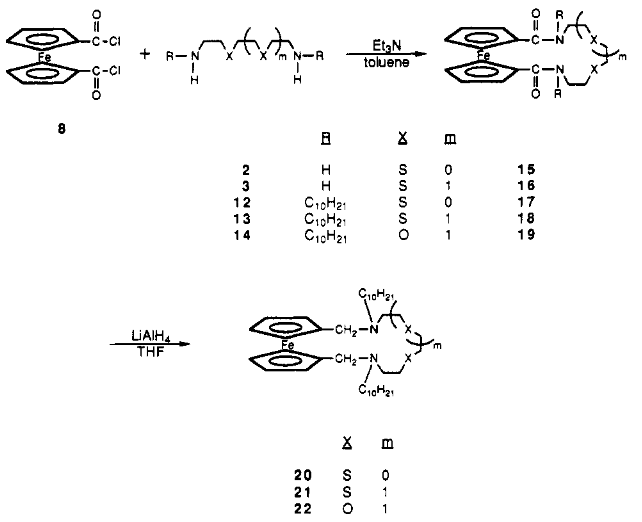
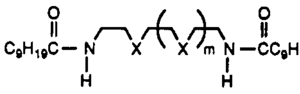
Scheme II



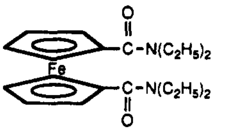
	R	X	m	
2	H	S	0	**15**
3	H	S	1	**16**
12	$C_{10}H_{21}$	S	0	**17**
13	$C_{10}H_{21}$	S	1	**18**
14	$C_{10}H_{21}$	O	1	**19**

	X	m
20	S	0
21	S	1
22	O	1

ethylamine, ferrocenophane diamides **15** and **16** were obtained in 13 and 27% yields, respectively (Scheme II). The cyclization yield for **16** is identical with that reported,[7] but more supportive elemental analysis data were obtained in the present study. Due to the extremely poor solubilities of **15** and **16** in solvents that would be suitable for reduction reactions, attempts to prepare the corresponding ferrocenophane diamines were abandoned. To overcome the solubility problem, lipophilic thiadiamine **12** and dithiadiamine **13** were synthesized. Thus acylation of thiadiamine **2** with decanoyl chloride gave thiadiamide **9** in 60% yield. Reduction of **9** with lithium aluminum hydride in tetrahydrofuran gave lipophilic thiadiamine **12** in 84% yield. An analogous reaction sequence led from dithiadiamine **3** to dithiadiamide **10** (91% yield), which was subsequently reduced to lipophilic dithiadiamine **13** (85% yield). High-dilution cyclizations of these lipophilic diamines with 1,1′-bis(chlorocarbonyl)ferrocene (**8**) provided the lipophilic ferrocenophane thiadiamide **17** and dithiadiamide **18** in 22 and 55% yields, respectively. Reduction of diamides **17** and **18** with lithium aluminum hydride in tetrahydrofuran provided diazathiaferrocenophanes **20** and diazadithiaferrocenophane **21** and 53 and 77% yields, respectively.



	X	m
9	S	0
10	S	1
11	O	1



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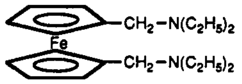

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The diazadioxaferrocenophane **22** was synthesized in a similar manner. The requisite lipophilic diamide **11** was prepared from 3,6-dioxa-1,8-diaminooctane[15] and decanoyl chloride in 88% yield. Reduction of **11** with lithium aluminum hydride in tetrahydrofuran gave the lipophilic diamine **14** in 88% yield. Cyclic diamide **19** was obtained by reaction of 1,1′-bis(chlorocarbonyl)ferrocene (**8**) and diamine **14** in 46% yield. Subsequent reduction of ferrocenophane diamide **19** afforded diazadioxaferrocenophane **22** in 53% yield. A model, acyclic ferrocene diamine **24**, was obtained from diacid chloride **8** and diethylamine via diamide **23**[17] (91% yield) followed by reduction with lithium aluminum hydride (52% yield).

Table I. Electrochemical Parameters of Ferrocenophanes and Related Compounds[a]

compd	$E_{1/2}$, mV vs SHE	ΔE_p, mV
5	553	67
6	376	71
7	366	75
18	674	106
19	634	71
20	705	75
21	727	83
22[b]	369	83
24	359	126
Fc-1,1′-$(CO_2H)_2$	805	75

[a] 25.0 °C, 0.1 M NBu_4ClO_4 (CH_3CN). Pt working and auxiliary electrodes, SCE reference electrode in aqueous 0.1 M $NaNO_3$. Sweep rate 50 mV/s. Uncertainty in $E_{1/2}$ estimated at ±5 mV. $E_{1/2}$ calculated as $(E_{pa} + E_{pc})/2$ and referenced to SHE with hydroxyethylferrocene internal calibrant. [b] Voltammograms degraded rapidly in steady-state sweeps, indicating that the primary oxidation product adheres to the Pt electrode. In addition to the reversible response with $E_{1/2}$ = 369 mV, **22** exhibits a very broad, irreversible anodic wave with $E_{pa} \approx 1.2$ V.

New compounds **4**–**7**, **12**–**22**, and **24** were fully characterized by NMR and IR spectra and by elemental analysis. Due to the extremely poor solubility of lipophilic acyclic diamides **9**–**11** it was not possible to obtain NMR spectra so characterization was by IR spectra and elemental analysis.

Electrochemistry. Half-wave potentials and peak-to-peak separations derived from cyclic voltammograms of azathiaferrocenophanes, azaoxaferrocenophanes, acyclic analogues and model compounds at 25.0 °C in acetonitrile solution (0.1 M TBAP) are summarzied in Table I. The upper and lower $E_{1/2}$ limits of 805 and 359 mV vs SHE are defined by 1,1′-ferrocenedicarboxylic acid and 1,1′-bis(diethylaminomethyl)ferrocene (**24**), respectively.

The acyclic thiadiamine and dithiadiamine bis(ferrocenyl) compounds, **6** and **7**, respectively, exhibit essentially identical half-wave potentials, which are quite similar to that of 1,1′-bis(diethylaminomethyl)ferrocene (**24**). The oxidation wave of **5**, the dithiadiamide precursor to **7**, is displaced by 187 mV to a more positive potential, as would be anticipated from the well-established inductive effects of the ferrocene acyl and alkyl substituents.[18,19] In general, ferrocenium/ferrocene half-wave potentials correlate well with Hammett constants for groups attached directly to the cyclopentadienyl rings or to phenyl substituents.[20,21]

The half-wave reduction potentials of the ferrocenium ions derived from azathiaferrocenophanes **20** and **21** are 0.3 V more positive than those for the acyclic analogues **6** and **7**. In further contrast with the acyclic analogues **5**–**7**, the Fe(III,II) $E_{1/2}$ values for **20** and **21** are shifted *anodically* with respect to that for **18**, the dithiadiamide precusor to **21**.

Ferrocenophanes with 2,8-dithia-5-oxa[9](1,1′), 2,11-dithia-5,8-dioxa[12](1,1′), and 2,14-dithia-5,8,11-trioxa-

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[15](1,1′) bridging chains are characterized by Fe(III,II) $E_{1/2}$ values in a narrow range (405,[1] 419,[1] and 416[22] mV, respectively), which is effectively independent of the chain length and number of ring oxygens. In agreement, the half-wave reduction potentials for azathiaferrocenophanes **20** and **21** are quite similar to each other, which demonstrates that the bridging chain length is not a determining factor in the redox thermodynamics.

The structures of diazadithiaferrocenophane **21** and its diamide precursor **18** are the same as those for diazadioxaferrocenophane **22** and its diamide precursor **19**, except for replacement of the two ring sulfur atoms in the former pair with two ring oxygen atoms in the latter pair. The half-wave potentials for the diamide precursors **18** and **19** differ by only 40 mV. However, the $E_{1/2}$ value for diazadithiaferrocenophane **21** is 350 mV more positive than that for diazadioxaferrocenophane **22**. Thus the preferential stabilization of the Fe(II) oxidation state by the thioether sulfur atoms becomes effective only when the hybridization of carbon atoms 1 and 12 is changed from sp^2 to sp^3.

The Fe(III,II) reduction potential of ferrocene derivatives is influenced not only by cyclopentadienyl rings substituents, but also by tilting of the Cp^- rings from a parallel orientation, preferential solvation of the ferrocenium forms, and the proximity of cations to the iron atom.[23-26] On consideration of our previously reported X-ray crystal structure and $E_{1/2}$ value of 2,11-dithia-5,8-dioxa[12](1,1′)ferrocenophane,[1] there is no reason to suspect that any of these factors contributes significantly to the unusually positive $E_{1/2}$ value of **21**. The ground-state electronic term of the ferrocenium cation is generally thought to be $^2E_{2g}$ (D_5), derived from the $a_{1g}{}^2e_{2g}{}^3$ electronic configuration of the two highest energy occupied molecular orbitals.[24,25,27] Although this term is split into a pair of Kramers doublets by the combined action of spin–orbit coupling and low-symmetry crystal fields (including Jahn–Teller distortion), large orbital contributions to the ferrocenium cation effective magnetic moment and magnetic *g* factor reveal that such splitting is not large in the solid state.[25,27] More substantial distortion of the ferrocenium cation in solution is revealed by both NMR evidence and reductions in the effective magnetic moment toward the spin-only value.[25] However, theoretical considerations[24] suggest that bending of the ferrocene Cp^- rings should drive the $E_{1/2}$ value to a less positive potential, such that another source of Fe(II) stabilization must be sought to account for the $E_{1/2}$ values of **20** and **21** regardless of any structural distortion that may be induced by the ferrocenophane linking chains. Similarly, the possibility of redox-induced cyclopentadienyl ring rotation from an eclipsed to a staggered configuration cannot be ruled out, but the contribution of such a minor structural change to the energetics of ferrocenium reduction is expected to be negligibly small.[28,29]

The exceptionally favorable half-wave reduction potentials of the one-electron oxidation products of azathiaferrocenophanes **20** and **21** are most simply accounted for in terms of a strong bonding interaction between a thioether S atom and the ferrocene e_{2g} HOMO, which typically is a nonbonding, Fe-centered set composed of the $3d_{xy}$ and $3d_{x^2-y^2}$ atomic orbitals.[24] Crown thioethers are known to induce unusual electronic and redox behavior,[12] including the stabilization of low oxidation states in Cu(I)[30,31] and Ru(II)[32] complexes, the latter having the same d^6 electronic configuration as Fe(II). Such stabilization has been attributed to the affinity of low-valent metal ions for the "soft" thioether sulfur donor atom or to a M($d\pi$)-to-S($3d\pi$) back-bonding interaction analogous to that thought to be responsible for the strong bonds formed between low oxidation state metal centers and phosphine π-accepting ligands.[33] Molecular orbital calculations on Cu(I)–thioether S complexes suggest that the unoccupied sulfur 3d LUMO orbitals lie only 3–5 eV higher in energy than the filled metal HOMO 3d set, permitting substantial stabilization of the HOMO by mixing in of sulfur 3d orbital character.[34] Although few model Fe(II)–thioether complexes have been reported,[33] the 30–150-mV increase in E°[Fe(III,II)] associated with the substitution of histidine, imidazole or lysine ϵ-amino nitrogen atoms by methionine sulfur in c-type cytochromes is well-established.[35,36] Neutralization of formal positive charge in a medium of low dielectric constant is also thought to promote the conversion of heme-ligated Fe(III) to Fe(II),[37] but the importance of such an effect in the present instance of thioether S-promoted reduction is ruled out by the fact that ferrocenophanes **21** and **22** contain identical *N*-decyl substituents, but the $E_{1/2}$ value of the diazadioxa compound is scarcely enhanced relative to that of model compound **24**.

A CPK space-filling molecular model of **21** reveals a steric constraint that only one of the two sulfur atoms may occupy an equatorial coordination position at one time, consistent with the finding that the half-wave potential of diazathiaferrocenophane **20** is only 22 mV smaller than that of diazathiaferrocenophane **21**. Indeed, the propensity of crown thioethers for gauche placement at the C–S bonds typically brings about both exo and endo sulfur atom orientations relative to the macrocyclic ring.[38]

Carbon-13 chemical shift comparisons demonstrate that a methylthio group attached directly to a ferrocene cyclopentadienyl ring is electronegative, presumably through an electron-withdrawing C($p\pi$)–S($d\pi$) interaction, in contrast to the behavior of the $-SCH_3$ function in thioanisole.[23] Both inductive and through-space interactions of 1- and 3-position chalcogen atoms with the Fe center in trichalcogena[3]ferrocenophanes have been proposed to account for exceptionally positive half-wave potentials of these species.[9] The sulfur substituents of 1,*n*-dithia[*n*]ferrocenophanes (*n* = 4–8, 10) have an opposite effect to those of azathiaferrocenophanes **20** and **21**, shifting the $E_{1/2}$ value to more negative potentials by increments that are highly sensitive to the bridging chain length; i.e., for *n* =

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4 and 7, $E_{1/2}$ = 0.27 and −0.04 V vs Ag/AgNO$_3$ (0.05 M), respectively.[23] Elevation of the HOMO level is attributed to the influence of sulfur 3p lone pairs oriented toward the iron $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals. Thus, S atoms directly attached to ferrocene cyclopentadienyl rings are incapable of a HOMO-stabilizing Fe(dπ)–S(dπ) overlap of the type proposed here for the 2,8-diaza-5-thia[9](1,1′)- and 2,11-diaza-5,8-dithia[12](1,1′)ferrocenophanes **20** and **21**, respectively.

Experimental Section

General Data. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 267 spectrophotometer and are reported in reciprocal centimeters. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300-MHz or a Varian Gemini 200-MHz spectrometer, and chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Elemental analysis was performed by Spang Laboratories of Eagle Harbor, MI, and Desert Analytics of Tucson, AZ.

Materials. Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. Tetrahydrofuran was distilled from benzophenone ketyl. Ferrocenoyl chloride[13] (**1**), 1,1′-bis(chlorocarbonyl)ferrocene[16] (**8**), 3-thia-1,5-diaminopentane[14] (**2**), and 3,6-dithia-1,8-diaminooctane[15] (**3**) were prepared according to the literature procedures.

Preparation of Acyclic Diamides 4 and 5. A solution of ferrocenoyl chloride (**1**) (2.00 g, 8.05 mmol) in toluene (80 mL) was added dropwise to a solution of the corresponding diamine (4.02 mmol) and triethylamine (1.4 mL) in toluene (40 mL) at 0–5 °C under argon, and the mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was dissolved in chloroform. The solution was filtered through a layer of alumina and subjected to column chromatography on silica gel with CHCl$_3$–EtOH (20:1) as eluent to give the diamide.

4: 72% yield; orange, amorphous solid with mp 196–197 °C; ^{1}H NMR (DMSO-d_6) δ 2.72 (t, 4 H, CH_2S), 3.37 (t, 4 H, CH_2N), 4.17 (s, 10 H, FcH), 4.78 (t, 4 H, FcH), 7.97 (t, 2 H, NH), 8.31 (s, 1 H, CHCl$_3$); ^{13}C NMR (DMSO-d_6) δ 30.87 (CH$_2$S), 38.80 (CH$_2$N), 68.27, 69.54, 70.05, and 76.68 (Fc), 79.35 (CHCl$_3$), 169.45 (C=O); IR (Nujol) 3270 (N—H), 1630 (C=O) cm^{-1}. Anal. Calcd for $C_{26}H_{28}Fe_2N_2O_2S$: C, 57.38; H, 5.19. Found: C, 57.10; H, 5.31.

5: 67% yield; orange, amorphous solid with mp 170–171 °C; ^{1}H NMR (DMSO-d_6) δ 2.70 (t, 4 H, CH_2S), 2.79 (s, 4 H, CH_2S), 3.34 (t, 4 H CH_2N), 4.17 (s, 10 H, FcH), 4.33 (t, 4 H, FcH), 4.76 (t, 4 H, FcH), 7.98 (t, 2 H, NH); ^{13}C NMR (DMSO-d_6) δ 30.59 and 31.01 (CH$_2$S), 38.77 (CH$_2$N), 68.25, 69.56, 70.11, and 76.54 (Fc), 169.61 (C=O); IR (Nujol) 3340 (N—H), 1625 (C=O) cm^{-1}. Anal. Calcd for $C_{28}H_{32}Fe_2N_2O_2S_2$: C, 55.64; H, 5.34. Found: C, 55.73; H, 5.35.

Preparation of Acyclic Diamines 6 and 7. The diamide (0.68 mmol) was added in small portions to a suspension of LiAlH$_4$ (1.33 g, 35.0 mmol) in dry THF (28 mL), and the mixture was refluxed for 15 h. After cooling with an ice bath, the reaction mixture was quenched by subsequent additions of aqueous THF (0.85 mL of H$_2$O and 2.9 mL of THF), 15% aqueous NaOH (1.6 mL), and aqueous THF again (2.6 mL of H$_2$O and 4.3 mL of THF). The insoluble material was filtered and washed with THF. The combined organic solutions were evaporated in vacuo, and the residue was purified by column chromatography on silica gel with CHCl$_3$–EtOH (10:1) as eluent to afford the diamine.

6: 78% yield; yellow solid with mp 61–63 °C, ^{1}H NMR (CDCl$_3$) δ 2.63 (br s, 2 H, NH), 2.68 (t, 4 H, CH_2S), 2.82 (t, 4 H, CH_2N), 3.51 (s, 4 H, FcCH_2), 4.11 (t, 4 H, FcH), 4.13 (s, 10 H, FcH), 4.18 (t, 4 H, FcH); ^{13}C NMR (CDCl$_3$) δ 31.82 (CH$_2$S), 47.92 and 48.41 (CH_2N), 67.86, 68.41, and 85.96 (Fc[39]); IR (deposit on NaCl plate) 3300 (N–H) cm^{-1}. Anal. Calcd for $C_{26}H_{32}Fe_2N_2S$: C, 60.48; H, 6.25. Found: C, 60.49; H, 6.25.

7: 62% yield; yellow crystals with mp 35–37 °C (from Et$_2$O); ^{1}H NMR (CDCl$_3$) δ 1.82 (br s, 2 H, NH), 2.68–2.74 (m, 8 H, CH_2S), 2.80–2.86 (m, 4 H, CH_2N), 3.52 (s, 4 H, FcCH_2), 4.10 (t, 4 H, FcH), 4.14 (s, 10 H, FcH), 4.18 (t, 4 H, FcH); ^{13}C NMR (CDCl$_3$) δ 31.97 and 32.45 (CH$_2$S), 48.02 and 48.60 (CH$_2$N), 67.79, 68.28, 68.40, and 86.67 (Fc); IR (film) 3310 (N–H) cm^{-1}. Anal. Calcd for $C_{28}H_{36}Fe_2N_2S_2$: C, 58.34; H, 6.29. Found: 58.09; H, 6.20.

Preparation of Lipophilic Diamides 9–11. A solution of decanoyl chloride (6.52 g, 34.2 mmol) in THF (20 mL) was added dropwise to a solution of the appropriate diamine (17.0 mmol) and triethylamine (4.33 g, 42.8 mmol) in THF (20 mL). After stirring for 12 h at room temperature, the reaction mixture was filtered and the solid was washed with large amounts of water and anhydrous Et$_2$O. Drying under vacuum at 60 °C gave the diamide.

9: 60% yield; white, waxy solid with mp 133–134 °C; IR (KBr) 3296 (N—H), 1631 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{48}N_2O_2S{\cdot}0.5H_2O$: C, 65.85; H, 11.28. Found: C, 66.15; H, 11.28.

10: 91% yield; white waxy solid with mp 150–152 °C; IR (KBr) 3241 (N—H), 1635 (C=O) cm^{-1}. Anal. Calcd for $C_{26}H_{52}N_2O_2S_2{\cdot}0.5H_2O$: C, 62.73; H, 10.73. Found: C, 63.11; H, 10.98.

11: 88% yield; white waxy solid with mp 110–112 °C; IR (KBr) 3280 (N—H), 1639 (C=O) cm^{-1}. Anal. Calcd for $C_{26}H_{52}N_2O_4$: C, 68.38; H, 11.48. Found: C, 68.48; H, 11.44.

Preparation of Lipophilic Acyclic Diamines 12–14. A suspension of LiAlH$_4$ (1.55 g, 40.9 mmol) in THF (100 mL) was added dropwise to a suspension of the appropriate diamide (8.18 mmol) in THF (400 mL), and the mixture was refluxed for 48 h. The reaction mixture was cooled and aqueous 5% NaOH was added slowly. After stirring for 3 h, the mixture was filtered and the solvent was removed in vacuo. The residue was passed through a short bed of alumina with CH$_2$Cl$_2$ as eluent to give the diamine.

12: 84% yield; white, waxy solid with mp 25–26 °C; ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 6 H, CH_3), 1.26–1.48 (m, 34 H, NH + CH_2), 2.57–2.71 (m, 8 H, CH_2N), 2.78 (t, 4 H, CH_2S); IR (KBr) 3262 (N–H) cm^{-1}. Anal. Calcd for $C_{24}H_{52}N_2S$: C, 71.93; H, 13.08. Found: C, 72.12; H, 13.26.

13: 85% yield; white, waxy solid with mp 57–58 °C; ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 6 H, CH_3), 1.27–1.49 (m, 34 H, NH + CH_2), 2.57–2.85 (m, 6 H, CH_2N + CH_2S); IR (KBr) 3299 (N–H) cm^{-1}. Anal. Calcd for $C_{26}H_{56}N_2S_2{\cdot}0.1CH_2Cl_2$: C, 66.70; H, 12.10. Found: C, 66.35; H, 12.30.

14: 88% yield; white, waxy solid with mp 29–30 °C; ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 6 H, CH_3), 1.26–1.52 (m, 32 H, CH_2), 1.77 (br s, 2 H, NH), 2.60 (t, CH_2N), 2.79 (t, 4 H, CH_2N), 3.57–3.62 (m, 8 H, CH_2O); IR (KBr) 3320 (N–H) cm^{-1}. Anal. Calcd for $C_{26}H_{56}N_2O_2$: C, 72.84; H, 13.17. Found: C, 73.18, H, 13.48.

Preparation of Ferrocenophane Diamides 15–19. Solution A (320 mL) was prepared by dissolving 1,1′-bis(chlorocarbonyl)ferrocene (**8**) (2.34 g, 7.53 mmol) in benzene. Triethylamine (2.4 mL) and the appropriate diamine (7.53 mmol) were dissolved in benzene to make 320 mL of solution B. Solutions A and B were added simultaneously over 4 h to 320 mL of vigorously stirred benzene, under argon. The reaction mixture was stirred overnight at room temperature, the solvent was removed in vacuo, and the residue was purified by column chromatography to afford the diamide.

15: 13% yield after chromatography on silica gel with CHCl$_3$–C$_2$H$_5$OH (9:1) as eluent; orange solid with mp 185 °C (dec); ^{1}H NMR (DMSO-d_6) δ 2.75 (deformed t, 4 H, CH_2S), 3.34 (deformed t, 4 H, CH_2N), 4.41 (br s, 4 H, FcH), 4.63 (br s, 4 H, FcH), 7.69 (t, 2 H, NH); ^{13}C NMR (DMSO-d_6) δ 31.16 (CH$_2$S), 38.39 (CH$_2$N), 70.32, 70.44, and 78.55 (Fc), 168.56 (C=O). Anal. Calcd for $C_{16}H_{18}FeN_2O_2S$: C, 53.64; H, 5.06. Found: C, 53.82; H, 4.89.

16: 27% yield after chromatography on silica gel with CHCl$_3$–EtOH (49:1→19:1) and then CH$_2$Cl$_2$–MeOH (49:1→19:1) as eluents; orange solid with mp 188 °C (dec); ^{1}H NMR (DMSO-d_6): δ 2.77 (t, 4 H, CH_2S), 2.87 (s, 4 H, CH_2S), 3.34 (t, 4 H, CH_2N), 4.38 (t, 4 H, FcH), 4.74 (t, 4 H, FcH), 8.02 (t, 2 H, NH). ^{13}C NMR (DMSO-d_6) δ 30.03 and 30.81 (CH$_2$S), 39.30 (CH$_2$N), 69.50, 70.35, and 79.08 (Fc), 168.24 (C=O); IR (Nujol) 3220 (N—H), 1635, 1620 (C=O) cm^{-1}. Anal. Calcd for $C_{18}H_{22}FeN_2O_2S_2$: C, 51.68; H, 5.30. Found: C, 51.80; H, 5.27.

17: 22% yield after chromatography on silica gel with petroleum ether–EtOAc (2:1) as eluent; orange solid with mp 97–99 °C; ^{1}H NMR (CDCl$_3$) δ 0.85 (t, 6 H, CH_3), 1.05–1.65 (m, 32 H,

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[39] The absorption at 68.41 δ results from exact overlap of the signal from the unsubstituted Cp ring carbons and that from one of the substituted ring carbons.

C*H*$_2$), 2.55–2.95 (m, 4 H, C*H*$_2$S), 3.30–3.70 (m, 8 H, C*H*$_2$N), 4.38 (s, 4 H, Fc*H*), 4.58 (s, 4 H, Fc*H*); ^{13}C NMR (CDCl$_3$) δ 14.30 (*C*H$_3$), 22.88, 26.99, 27.36, 29.53, 29.63, 29.78, 29.86, 32.12 (*C*H$_2$), 27.98, 30.78 (*C*H$_2$S), 47.32, 48.72, 49.83 (*C*H$_2$N), 70.37, 71.56, 72.67 (broad overlapping signals), 81.5 (broad signal) (Fc), 170.13 (C=O); IR (film) 1615 (C=O) cm^{-1}. Anal. Calcd for $C_{36}H_{58}FeN_2O_2S$: C, 67.69; H, 9.15. Found: C, 67.74; H, 8.96.

18: 55% yield after chromatography on basic alumina with petroleum ether–EtOAc (5:1) as eluent; orange crystals with mp 59.5–61 °C; ^{1}H NMR (CDCl$_3$) δ 0.85 (t, 6 H, C*H*$_3$), 1.00–1.65 (m, 32 H, C*H*$_2$), 2.70–3.80 (m, 16 H, C*H*$_2$S + C*H*$_2$N), 4.20–4.75 (m, 8 H, Fc*H*); ^{13}C NMR (CDCl$_3$) δ 14.27 (*C*H$_3$), 22.85, 26.77, 27.33, 29.29, 29.47, 29.70, 30.32, 30.75, 31.04, 32.08, 32.47, 33.18 (*C*H$_2$ and *C*H$_2$S), 46.61, 47.48, 49.29, 50.06 (*C*H$_2$N), 69.36, 70.49, 71.49, 72.16, 72.92, 74.83, 83.37 (Fc), 169.37 (C=O); IR (film) 1612 (C=O) cm^{-1}. Anal. Calcd for $C_{38}H_{62}FeN_2O_2S_2$: C, 65.31; H, 8.94. Found: C, 65,56; H, 8.66.

19: 46% yield after chromatography on basic alumina with petroleum ether–EtOAc (1:1) as eluent; tan crystals with mp 59.5–61.5 °C; ^{1}H NMR (CDCl$_3$) δ 0.84 (t, 6 H, C*H*$_3$), 1.05–1.65 (m, 32 H, C*H*$_2$), 3.25–3.85 (m, 16 H, C*H*$_2$N + C*H*$_2$O), 4.25–4.75 (m, 8 H, Fc); ^{13}C NMR (CDCl$_3$) δ 14.29 (*C*H$_3$), 22.88, 26.92, 27.21, 27.49, 29.72, 29.82, 29.91, 32.13 (*C*H$_2$), 45.94, 47.85, 48.76, 50.20 (*C*H$_2$N), 68.50, 69.36, 70.47, 70.97, 71.67, 72.58, 74.03, 83.86 (*C*H$_2$O + Fc), 170.52 (*C*=O); IR (film) 1612 (C=O), 1127 (C—O) cm^{-1}. Anal. Calcd for $C_{38}H_{62}FeN_2O_4$: C, 68.45; H, 9.37. Found: C, 68.32; H, 9.41.

Preparation of Ferrocenophane Diamines 20–22. The appropriate ferrocenophane diamide (1.05 mmol) was added to a suspension of LiAlH$_4$ (0.20 g, 5.42 mmol) in dry THF (30 mL). The heterogeneous mixture was stirred at room temperature for 3 days. EtOAc (20 mL) and a few drops of water were added and the organic layer was decanted, dried over anhydrous K$_2$CO$_3$, and evaporated in vacuo. The residue was purified by column chromatography to give the ferrocenophane diamine.

20: 53% yield after chromatography on basic alumina with petroleum ether–EtOAc (10:1) as eluent; orange crystals with mp 59–60.5 °C; ^{1}H NMR (CDCl$_3$) δ 0.85 (t, 6 H, C*H*$_3$), 1.10–1.50 (m, 32 H, C*H*$_2$), 2.31 (t, 4 H, RC*H*$_2$N), 2.55 (s, 8 H, SC*H*$_2$C*H*$_2$N), 3.50 (s, 4 H, FcC*H*$_2$), 4.05–4.13 (m, 8 H, Fc*H*); ^{13}C NMR (CDCl$_3$) δ 14.31 (*C*H$_3$), 22.89, 27.51, 27.69, 29.56, 29.82, 29.89, 30.28 (*C*H$_2$), 32.15 (*C*H$_2$S), 53.41, 53.72, 53.84 (*C*H$_2$N), 68.99, 70.98, 83.64 (Fc). Anal. Calcd for $C_{36}H_{62}FeN_2S$: C, 70.79; H, 10.23. Found: C, 70.51; H, 10.30.

21: 77% yield after chromatography on basic alumina with petroleum ether–EtOAc (5:1) as eluent; orange crystals with mp 47–49 °C; ^{1}H NMR (CDCl$_3$) δ 0.85 (t, 6 H, C*H*$_3$), 1.00–1.40 (m, 32 H, C*H*$_2$), 2.26 (t, 4 H RC*H*$_2$N), 2.70 (s, 8 H NC*H*H$_2$C*H*$_2$S), 2.77 (s, 4 H, SC*H*$_2$C*H*$_2$S), 3.48 (s, 4 H, FcC*H*$_2$), 4.00–4.12 (m, 8 H, Fc*H*); ^{13}C NMR (CDCl$_3$) δ 14.28 (*C*H$_3$), 22.86, 27.07, 27.51, 29.52, 29.68, 29.79, 29.87 (*C*H$_2$), 32.11, 32.99 (*C*H$_2$S), 53.14, 53.57, 54.84 (*C*H$_2$N), 68.27, 71.16, and 84.40 (Fc). Anal. Calcd for $C_{38}H_{66}FeN_2S_2$: C, 68.03; H, 9.91. Found: C, 68.12; H, 9.96.

22: 53% yield after chromatography on deactivated, basic alumina with petroleum ether–EtOAc (2:1) as eluent; light brown oil; ^{1}H NMR (CDCl$_3$) δ 0.84 (t, 6 H, C*H*$_3$), 1.05–1.40 (m, 32 H, C*H*$_2$), 2.23 (t, 4 H, C*H*$_2$N), 2.64 (t, 4 H, C*H*$_2$N), 3.55–3.70 (m, 12 H, C*H*$_2$O + FcC*H*$_2$), 4.04 (s, 8 H, Fc*H*); ^{13}C NMR (CDCl$_3$) 14.31 (*C*H$_3$), 22.88, 27.15, 27.68, 29.54, 29.78, 32.13 (*C*H$_2$), 52.52, 53.49, 53.99 (*C*H$_2$N), 68.07, 71.68 (*C*H$_2$O), 71.11, 72.92, 84.10 (Fc); IR (neat): 1118 (C–O) cm^{-1}. Anal. Calcd for $C_{38}H_{66}FeN_2O_2$: C, 71.45; H, 10.41. Found: C, 71.49; H, 10.51.

Preparation of Diamine 24. A mixture of 1,1′-bis[(diethylamino)carbonyl]ferrocene[17] (**23**) (0.50 g, 1.30 mmol) and LiAlH$_4$ (0.25 g, 6.59 mmol) in THF (30 mL) was stirred for 2 days and worked up in the manner described above for the preparation of ferrocenophanes **20–22** to give, after chromatography on basic alumina with EtOAc as eluent, diamine **24** (0.24 g, 54%) as a light brown oil: ^{1}H NMR (CDCl$_3$): δ 1.00 (t, 12 H, C*H*$_3$), 2.39 (q, 8 H, C*H*$_2$N), 3.46 (s, 4 H, FcC*H*$_2$), 4.03 (br s, 8 H, Fc*H*); ^{13}C NMR (CDCl$_3$) δ 12.19 (*C*H$_3$), 46.45 (*C*H$_2$N), 51.93 (Fc*C*H$_2$), 68.73, 71.03, 83.32 (Fc). Anal. Calcd for $C_{20}H_{32}FeN_2$: C, 67.42; H, 9.05. Found: C, 67.35; H, 9.12.

Cyclic Voltammetry. Cyclic voltammetric measurements were performed as before[1] on 1 mM or saturated solutions of electroactive solutes in acetronitrile (25.0 °C, 0.1 M NBu$_4$ClO$_4$ supporting electrolyte, Pt working and auxiliary electrodes, SCE reference electrode in aqueous 0.1 M NaNO$_3$). Reversibility was established through determinations of the anodic peak current as a function of sweep rate (50–300 mV/s) and the i_{pa}/i_{pc} ratio. Reported half-wave potentials were calculated as the average of anodic and cathodic peak potentials when the $E_{1/2}$ value exhibited no sweep rate dependence in the 50–300 mV/s range; conversion to the SHE scale was accomplished by using hydroxyethylferrocene ($E_{1/2}$ = 402 mV vs SHE) as an internal calibrant.

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